

Clusters, phason elasticity, and entropic stabilization: a theory perspective

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1. Introduction

My viewpoint comes from a bottom-up approach to modeling quasicrystal structure and explaining their thermodynamic stabilization. That is, we start with ab-initio or pair potential based evaluation of the total energy, to capture the $T=0$ behavior; or perhaps MD (Molecular Dynamics) and MC (Monte Carlo) simulation for $T > 0$. We inductively identify motifs and restrict our model, so it has freedom to explore only the states we know are comparatively good. [At this level, the model may be formulated in terms of tilings or clusters, but the discrete geometry is just standing in as a way to label the distinct low-energy atomic configurations.] New simulations are constructed, which can handle larger length scales because there are fewer degrees of freedom. At the moment, this appears to be the most direct approach to ascertain whether energetic stabilization (e.g. an implementation of Penrose’s matching rules) is ever relevant to real quasicrystals.

1.1. Importance of using realistic potentials

In a metal, realistic pair potentials have Friedel oscillations [Fig. 1(a)]. I will review why this is the real-space analog of the ‘Hume-Rothery’ (and related) mechanisms in reciprocal space. The energy from second-order perturbation theory, computed in reciprocal space, is

$$\delta E = -\frac{1}{2} \sum_{\mathbf{q}} \sum_{\mathbf{G}} \frac{|\tilde{\phi}(\mathbf{G})|^2 |\tilde{\rho}(\mathbf{G})|^2}{E(\mathbf{q} + \mathbf{G}) - E(\mathbf{q})}, \quad (1)$$

where $E()$ is the free electron dispersion, and $\phi(\mathbf{r})$ is the [short ranged] potential for an atom to scatter an electron. [I do not encumber this illustration with multiple species.] So δE is most negative when $\tilde{\phi}(\mathbf{G})$, the atom density at the reciprocal lattice vector \mathbf{G} , is strong for \mathbf{G} nearly spanning the Fermi surface: Hume-Rothery’s criterion. If we now insert $\tilde{\rho}(\mathbf{q}) = \sum_i e^{i\mathbf{q} \cdot \mathbf{r}_i}$, where $\{\mathbf{r}_i\}$ are the atoms’ positions, we obtain

$$\delta E = \frac{1}{2} \sum_{ij} V_{\text{eff}}(\mathbf{r}_i - \mathbf{r}_j), \quad (2)$$

where the effective interatomic potential $V_{\text{eff}}()$ is the convolution of the electron susceptibility $\chi(r)$ with $\phi(r)$ twice. Since $\chi(q)$ has singularities in reciprocal space at $2k_F$, these appear as a factor $\propto \cos(2k_F r + \delta)$ in $\chi(r)$ – Friedel oscillations – which is inherited by $V_{\text{eff}}(r)$. Thus, Hume-Rothery stabilization is equivalent to saying the second or third minima in $V_{\text{eff}}(r)$ are important in determining the structure.

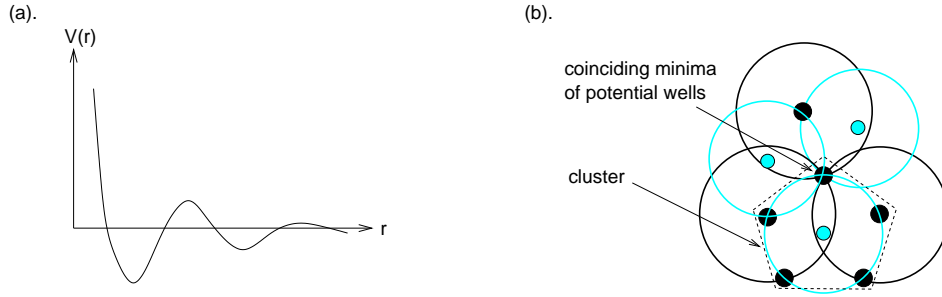


Figure 1. Long-range potentials and cluster stabilized from the outside. (b). A pentagonal cluster is outlined (dashed line) in a schematic model. Its topmost atom, is chosen for this example, lies at the bottom of potential wells (shown by circles) from five atoms inside the cluster, and three more atoms outside it.

At least, Friedel oscillations are important in the Al-TM family [i(AlPdMn), d(AlNiCo)] and in the Frank-Kasper family [i(ZnMgRE)]. In this conference, Mihalkovič and Widom [14] assert that the embedded-atom potentials [which lack Friedel oscillations, but implicitly include multi-atom interactions] work excellently for the i(CdCa) family.

As a result, the sites within a “cluster” are not governed by interactions with the other atoms in the cluster, but are a resultant of overlapping spheres representing the potential wells of second and third neighbor atoms, including those outside the cluster. This seemed to me the only explanation for the pseudo Mackay cluster in e.g. *i*-AlCuFe. [The outer shells have icosahedral symmetry, but the innermost one has a roughly 1/3 filling of 20 sites on 3-fold axes, where one geometrically would have expected an icosahedron].

1.2. Temperature does matter

The Al atoms have rather weak interactions, and sometimes seem to behave almost like a fluid moving around a framework of fixed and well-ordered TM atoms. Simulations by Widom, Cockayne [15], Mihalkovič [7], Gähler [16], and collaborators found frequent hoppings of the Al atoms, so that one wonders whether to speak of well-defined sites. The configurational entropy from this is obviously huge.

Simulation approaches have scarcely scratched the surface as far as addressing thermally excited disorder, but I would say we know what to do. The reason it has not been tried is that a thorough ab-initio-based study of a good quasicrystal has been carried out just a handful of times so far, and it is much simpler to do it at $T = 0$.

2. Clusters

The simulation experiences have led me to believe that in the known quasicrystals, clusters do not have physical reality (in the sense of having significantly stronger intra-cluster bonding). Yet clusters (or tiles, which I consider to be a closely related concept) are inescapable as a framework to organize our understanding of a structure.

A lesson we learned from more fundamental fields of 20th-century physics is that we all need frameworks to organize our thinking, but we forget it’s a coordinate system we impose to describe phenomena, not a physical reality. We should not be seduced

by our tools and ascribe fundamental significance to these mental constructs. Let us instead be open to “complementarity”: that is, dissimilar descriptions may secretly be equivalent.

2.1. Clusters for analyzing structures as predicted from energy calculations

Our experiences with decagonal structure models [6, 13] offer abundant examples in which the *same* structure may be expressed in terms of cluster C on network N , or of cluster C' on network N' . Perhaps cluster C' is related to C by some sort of inflation; or perhaps C' is associated with the voids in the packing of C and vice versa. (An example is the complementarity of Bergman clusters and Mackay clusters in icosahedral quasicrystals.)

In a great many models, the cluster is a mathematical corollary of a set of inequalities which express the energy minimization. This appears most baldly, perhaps, in abstract tiling models where one demands to maximize the frequency of occurrence of cluster M [1, 2, 4] – one presumably would say cluster M does have a physical content in this model. But in many cases, this optimization forces the presence of a much larger supertiling, and much larger clusters C appear at its vertices. Thus, the appearance of the cluster is dependent on things that happen far away: a slight change in e.g. stoichiometry, and the clusters which dominated the whole image may dissolve in favor of some other motif, as a consequence of delicately competing energies.

A second way in which the cluster configuration depends on faraway atoms can be seen in Al-TM quasicrystals, which are well described using pair potentials that have a strong second potential well due to Friedel oscillations. The fact that an atom occurs in a particular site within a cluster is then not mainly due to interactions with its neighbors in the cluster, but is the resultant of potentials from many more distant neighbors in the space surrounding the cluster, and which are sufficiently correlated that the potentials from them add constructively (see Fig. 1(b)).

In conclusion, my proposed operational definition of clusters is statistical: “a pattern of atoms which is found in all examples of a given ensemble.” An ensemble is implicit in anybody’s definition of a cluster: to locate the boundary around a group of atoms, it must be possible to surround the cluster in more than one way; one could not talk of e.g. the fcc lattice as being built from clusters. The implicit ensemble might be either multiple occurrences of the cluster in a large unit cell, or various crystal phases that contain the same cluster, or a single simulation cell in which one enumerates all the low-energy structures.

2.2. Clusters in cleavage and interfaces

One cannot rule out a cluster description a priori as a way to map the energy landscape of a structure. When I was more naive, in fact, I advanced a cluster model which assumed a certain cost of cutting the linkages between Mackay clusters along 2-fold and 3-fold symmetry directions, so as to predict the equilibrium crystal shape [5]. Although a certain knobbliness might be anticipated, still even if the crevices got filled by Al atoms the energy cost might still be a linear function of the cluster-cluster linkages cut by the placement of the interface.

But in view of the experience mentioned in Sec. 2.1, I no longer expect that cluster linkages govern the energy differences due to offsets or orientations of the interface. Nevertheless, one can imagine “clusters” emerging in the purely statistical

sense expressed in the “operational definition” at the end of Sec. 2.1. If a crack approaches similar groupings of atoms, presumably it tends to pass through them in similar fashions. Then the atoms which always find themselves together on the same side of the crack could be designated a “cluster” for the purposes of describing crack propagation. Notice that (i) such “clusters” need not be the same ones that are useful in describing the equilibrium ensemble (ii) one would expect their shape to have less symmetry than the material itself, as it must depend on the orientations of the crack propagation and of the crack shear. If it happens that in fact the *same* clusters appear in cracks of various orientations, and for other physically defined ensembles, that would be justification to attribute a ‘physical reality’ to the cluster – but such tests seem possible mainly in simulations, not in experiments.

3. Phason elasticity

My motivation here is not in the physical consequences of phason elasticity, but in using elasticity as an indicator of the nature of the quasicrystal state. *Gradient-squared* elastic free energies appear only in the *random-tiling* kind of phase, in the sense distinguished in Sec. 4, above. Matching-rule interactions would lead to an energy cost which is *linear* in the absolute value of phason strain components [8], presumably the same is true for any other interaction that has the same ground state (or to one in the same “local isomorphism” class).

[A small caveat should be offered. The linear cost is related to the discrete hops that are mathematically unavoidable in structures with the usual quasicrystal space groups [9]. On the other hand, for unusual non-symmorphic space groups, a “continuous phason mode” is possible [10] which *may* exhibit gradient-squared elasticity in the ground state, in the same sense that one-dimensional incommensurate crystals may. But no plausible atomic model structure of this class has ever been exhibited, much less a set of interactions for which it is the ground state.]

The experiments of de Boissieu *et al* on icosahedral phases are the only ones I know that support the validity of elastic theory and, implicitly, of a random-tiling-like equilibrium state. But I will not fully trust the elastic interpretation of the diffuse scattering until the quantitative elastic constants agree (at least in order of magnitude) with a plausible simulation. That has not happened yet: one reason is that the “canonical cell” tiling, which is the simplest way to make a well-specific ensemble for most cluster-based icosahedral models, is also the least tractable tiling to simulate; a second reason is that it is nontrivial to extract an absolute scale of fluctuations from measurements of diffuse scattering.

In the case of *decagonals*, no evidence of gradient-squared elasticity has ever been seen in experiments. The behavior of the entropic elastic theory in decagonal random tiling models is not well understood, either. Thus, it seems more plausible to me that matching rules (or the equivalent) are realized in decagonal quasicrystals, than in icosahedral ones.

4. Thermodynamic stabilization of quasicrystal phases

The two fundamental competing scenarios of the stabilization of quasicrystals are not exactly ‘entropy’ versus ‘energy’, as we often loosely say. Rather, the question is whether the model is in the qualitative class that contains quasiperiodic ideal tilings that have purely Bragg peaks, or the class that contains the maximally random tiling

in which long range order is an emergent phenomenon. This distinction is a rigorous one from the viewpoint of statistical mechanics, because these two states are separated by a phase transition, but that is of no help in distinguishing them experimentally.

4.1. Role of simulations

I have come to believe that ab-initio modeling, though tedious on account of the many levels of description between microscopic and macroscopic, [6, 7] is the quickest path to a solid understanding of which scenario should apply to a particular given material. It is sometimes objected that simulation is unfeasible for handling e.g. incommensurate modulations, when the effective repeat cell is far too large to simulate by brute force. But there are generally ways to bridge to large scales by connecting the simulations first to a kind of continuum model. [A valid analogy is that one can understand the geometry of a large soap bubble by evaluating its surface tension, which can be computed using a far smaller simulation cell.]

To get meaningful results, it is crucial (and very difficult) that the structure used in the modeling be made consistent with the Hamiltonian assumed – it must be the ground state (in the $T = 0$ case), or nearly so.

Rather generally, Al-TM quasicrystals seem to have a framework of well-fixed sites plus a scattering of sensitive sites. In *i*-AlMnSi (and perhaps some others), these are the δ atoms of Ref. [12], located on 6D body centers in the hyperspace formulation, or centering Bergman clusters in real space, which can alternate between Al or TM atoms or vacancies. In *d*-AlCoNi (Ni-rich or Co-rich), there are Al atoms in ‘channels’ [13] which undergo (in simulated models) intricate occupational/displacive orderings. At a higher level of description, such orderings can be expressed as terms – maybe the dominant terms – in the effective tile-tile interaction (whether or not it realizes matching rules).

4.2. Stoichiometry in random-tiling models?

It was asserted that ‘a considerable amount of chemical disorder is essential to a random-packing model. [3]’. Perhaps this is based on a mistaken picture that random packings (of clusters) necessarily create atom conflicts that must be resolved in a context-dependent way. But actually each *tile* in a tiling – whether random or governed by local rules – has a finite set of local environments, and the atom decoration is *designed* to fit well with every environment, without overlapping or conflicting atoms.

In the simplest cases – e.g. the square-triangle tiling with dodecagonal symmetry, or the rhombohedral tiling with ico symmetry – there are two kinds of tiles, and the (irrational) ratio of their numbers is fixed by the symmetry. The decoration is deterministic, so there is a unique stoichiometry. However, tilings related to real quasicrystals often have more than two tiles – e.g. the ‘canonical cell tiling’ with ico symmetry, or the ‘hexagon-boat-star’ with decagonal symmetry. Then within the sum rules fixed by symmetry, one kind of tile can be traded for a combination of the others; sometimes the decoration is such that this trade leaves the atom count unchanged [6], so our model is line compound in this case too. In the case that the atom content changed, though, the alloy composition would indeed be variable; but as Elser once suggested, such a decoration is undesirable since phason dynamics would be coupled to, and slowed by, mass diffusion, contrary to the observed relaxation in good quasicrystals.

4.3. Origin of matching rules?

Note that although it become attractive to reformulate matching rules in terms of a decoration that implements Gummelt-like covering rules, [3], I do not think this is likely to emerge from an atomistic model. If a covering cluster emerges, it will be a sort of accident from the maximization of some smaller non-overlapping cluster [see my comments on clusters in Sec. 2.1).]

Instead, I consider it much more likely that something similar in spirit to Penrose arrow rules emerges. That is, the larger energy scales expressed by the fundamental atomic sites define a random-tiling ensemble. Then additional occupational orderings in relatively rare sites define something like set of interacting arrows. In fact, Widom [11] (with Cockayne and Al-Lehyani) has found (in the past few years) a matching rule *almost* equivalent to Penrose's, in the decagonal $d(\text{AlCuCo})$, implemented in that case by an alternation AlCo/CoAl in the chemical occupancy of a pair.

4.4. Stabilization by which entropy?

The evidence is abundant that many quasicrystals are high-temperature phases, ergo stabilized by entropy – but, in many cases, not the tiling configurational entropy! for it is too small. So, the larger entropy of vibrations or of chemical disorder is the only candidate to affect the phase diagram. In the past, we brushed aside such entropy contributions, by claiming they must have a similar value in the quasicrystal phase as they do in the approximant phases. The latter phases were assumed to be the immediate competitors of the quasicrystal phase in the phase diagram, so the difference in vibrational or substitutional free energies would largely cancel. But perhaps we need to examine more carefully just how the quasicrystal ordering may affect these entropic terms.

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